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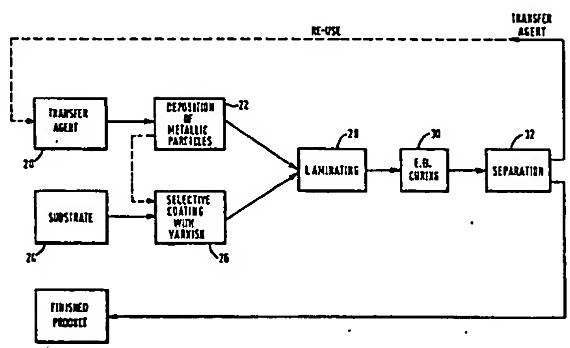
(54) Process for obtaining metallized surface using electron beam curing.

(57) A method of producing a specular metallic coating on a substrate using electron beam curing is described. The method basically comprises depositing (22) a thin metallic film on a transfer agent (20), applying (26) a coating of an electron beam-curable varnish to either the transfer agent (20) or a substrate (24), laminating (28) the metallized transfer agent and the substrate together before the varnish is cured, curing (30) the varnish using electron beam curing apparatus, and immediately delaminating (32) the transfer agent (20). The instantaneous curing has the advantages of speeding up the process and permitting uninterrupted flow of the metallized substrate for further processing.



PROCESS FOR OBTAINING METALLIZED SURFACE USING ELECTRON BEAM CURING

This invention relates generally to the metallization of a substrate and more specifically to a process for coating a substrate with a specular metallic coating using electron beam curing as one step in the process.

Various processes are known for the metallization of a substrate surface in web or sheet form. One such process involves the lamination of a thin metal foil to a substrate by the use of aqueous or non-aqueous solvent based adhesives. This process is commonly used for the metallization of paper or board and the most common metal used is aluminum foil. The thinnest commercially available foils have a thickness of 7 to 9μm. The gloss and finish of the final product depend not on the substrate but on the gloss and finish given to the foil during the lamination process. This process is disadvantageous from an economy viewpoint because the price of metal foil is high and a relatively thick coating is required.

Another commonly used process is vacuum metallization, wherein vaporized metal is condensed onto the substrate to be metallized. This procedure must take place in a vacuum on the order of 10^{-4} Torr

($1.33x10^{-2}$ Pa). It is only at these low pressures that the molecules of metallic vapor issuing from the evaporation source can reach the web without being blocked or oxidized by gases. Clearly, this process is well adapted to materials which will not degas or contain volatile substances such as moisture, plasticizers, monomers or residual solvents. Thus, the substrate used should typically be coated as the direct metallization of uncoated paper results in a poor finish. In order to improve the finish, it is necessary to prevarnish the paper substrate. Good results are obtained only if the paper is not too absorbent and if the prelaquer is very evenly distributed on the entire substrate surface.

Furthermore, when this process is applied to materials that substantially degas, such as paper and cardboard, vacuum metallization causes a loss of moisture content and subsequent permanent deformation of the substrate. Moreover, rehumidification may be required in order to avoid deterioration of the mechanical properties of the substrate.

Other processes which have been used in the past for coating surfaces include the so-called "transfer metallization" process described in U.S. Patent No.4,215,170 to Oliva. Briefly, this process involves coating a substrate or a transfer agent with varnish,

laminating the substrate and the transfer agent together before the varnish is dried, drying the varnish and separating the transfer agent from the substrate. The disclosure of U.S. Patent No. 4,215,170 is hereby incorporated by reference.

The Patent to Oliva discloses that the transfer agent which is used to carry and transfer metallizing agent may be either polypropylene, polyethylene, cellulose acetate, polyvinyl chloride, polyvinylidene chloride, regenerated cellulose and similar materials. The transfer metallization process sometimes involves a curing of the varnish which may require from 24 to 26 hours depending upon the ambient conditions. This curing time between lamination and separation interferes with immediate inspection and further treatment, such as slitting or printing, of the metallized products.

The search has continued for improved processes which require substantially less curing time. This invention was made as a result of that search.

Accordingly, a general object of the present invention is to avoid or substantially alleviate the above-mentioned problems of the prior art.

A more specific object of the present invention is to provide a process for coating a substrate wherein the drying time after lamination is minimized.

Another object of the present invention is to use electron beam curing in the metallization process in order to substantially reduce drying time in the final product.

Other objects and advantages of the present invention will become apparent from the following summary of the invention and description of its preferred embodiments.

The present invention provides a process for coating a substrate with a specular metallic coating and comprises:

(a) coating a transfer agent with a metallic coating;

(b) coating a portion of at least one of the substrate and the coated transfer agent with varnish;

(c) laminating the substrate and the transfer agent together before the varnish is cured;

(d) curing the varnish by using electron beam curing; and

(e) separating the transfer agent from the substrate.

The varnish coating may be applied to the entire surface or be selectively applied by gravure printing or the like.

The metallic film provides the substrate with the appearance of a specular metallic finish. The transfer agent may be reused in subsequent processes.

Furthermore, the coating and laminating steps may be carried out simultaneously.

The accompanying drawing is a flow diagram of the metallization process in accordance with the present invention.

The instant invention is directed to the process for the production of a metallic coated substrate through use of an electron beam curing technique. A transfer agent that has a glossy polished surface is metallized in a vacuum chamber. The transfer agent may be finely finished or may have a structured surface. The surface of the final product will be a replica of the surface of the transfer agent. The adhesion of the evaporated metal must be low and in particular less than that of the varnish to be employed. Suitable transfer agents include untreated polypropylene, polyethylene, polyvinyl chloride, regenerated cellulose, polyamide and release coated polyester films. Such transfer agents are disclosed in detail in U.S. Patent No. 4,215,170.

The transfer agent is metallized by any known technique such as vacuum metallization, chemical deposition or any other coating process. Suitable metals for deposition include aluminum, copper, silver, nickel, thin gold, their alloys and other vaporizable metals. The metal deposited will have a

thickness of generally less than about 1000Å (0.1μm), typically less than about 500Å (0.05μm), and preferably less than about 200Å (0.02μm). The quantity of metal deposited may be monitored by optical or resistance measurements. The variation of metal thickness across the width of the web should not fluctuate over too wide a range so that the final product will appear to have a homogeneous metallic surface.

The substrate which is to be coated with the metallic film may be in a web or sheet form and have a rough or smooth surface. Suitable substrates include any sheet material such as paper, cardboard, wood, leather and other fabrics.

Next a substrate is completely coated with varnish or selectively coated with varnish through use of method such as rotogravure, or lithography, flexography or other coating methods and the transfer agent is laminated to the substrate.

For some of the applicable coating processes, and in particular, for coating by the rotogravure process, the varnish is reduced with suitable solvents to create a predetermined viscosity for application with the coating equipment. In such cases, a drying step is added to the process to evaporate the solvents after application of the varnish. The varnish performs different functions during the transfer operation. The

varnish serves to level and smooth the surface of the substrate. The coating of the varnish may be applied over the metal deposited on the transfer film or on the substrate. It is also possible to use the laminating press to control directly the amount of varnish deposited.

The optimum amount of varnish that may be applied is readily determined by those skilled in this art. This amount varies depending upon the viscosity of the varnish, the degree to which the varnish is reduced with solvents, the pressure used during the lamination step, the hardness of the pressure rolls, and the porosity and surface irregularities of the substrate.

As noted above, when the varnish is reduced with a solvent, an additional station for drying is necessary to remove the solvent before lamination.

After the varnish is coated on the metallized surfaces or the substrate, a laminating step takes place before the varnish cures. The lamination is preferably carried out under slight pressure without heating the laminating rollers. The varnish will adhere to the metallized surface and will assume the surface characteristics on the transfer agent.

After lamination, the complex formed by the transfer agent and the substrate is passed through an electron beam curing apparatus as described below.

After curing, separation takes place. This step may take place immediately after curing due to the inherent advantages of the electron beam curing technique.

Separation substantially immediately after lamination is a great improvement over previous metallization processes which require long curing times. Immediate delamination allows immediate inspection of the final metallized product.

The transfer agent and substrate may be separated onto two separate rollers. After separation, the transfer agent may be reused numerous times, which is economically advantageous.

The finished product comprises a substrate which has a smooth specular metallic coating which appears to be continuous and smooth. This transfer technique may also be applied in cases where the varnish is deposited only on selected surfaces. Thus, only certain portions of the substrate would have a metallic appearance.

The coated substrate may also then be fed through additional printing stations rather than immediately rewound. The advantages of immediate curing are greatly utilized in such an instance. The advantages of immediate curing are particulary important if the printing of the varnish is done on the substrate in selective patterns, since printing in registration with those patterns can immediately be accomplished at the subsequent print stations.

The final product may be subject to various other processes such as cutting, embossing, die-stamping, slitting, lacquering and printing. These latter operations require usual techniques such as offset, rotogravure, flexography, silk screen and others which are all well-known to those skilled in this art.

The process and product of the instant invention will now be described in detail with reference to the figure.

The figure illustrates a block diagram of the process of the instant invention. Patent No. 4,215,170, which is incorporated herein by reference, differs in several important respects as will be described below. Transfer agent 20 is a plastic film which is preferably untreated polypropylene, or polyethylene polyester or polyvinyl chloride, and must be finely finished since it will impart the final surface to the metallized portions of the final product. The most efficient form of production of metallic coated surfaces occurs when transfer agent 20 is in the form of an elongated web of material which may be fed by roller means in accordance with the techniques described in U.S. Patent No. 4,215,170.

The transfer agent undergoes the step of metallic deposition at step 22 in accordance with the method of metallization described in detail in U.S. Patent No.

4,215,170. Briefly transfer agent 20 is fed into a conventional vacuum chamber where a metal such as aluminum is deposited upon the transfer agent. While thicker metallic coatings may be desirable for some applications, the resultant metallic film on the transfer agent preferably has a thickness of approximately 100Å to 500Å (0.01 to 0.05μm) and this extremely small thickness permits minimal use of metallic materials yet upon conclusion of the process gives the appearance of a completely metallized and continuous metal surface.

Substrate 24, the composition of which has been described above, may be in web or sheet form and have a rough or smooth surface. The substrate is completely coated or selectively coated with varnish at predetermined locations with gravure, lithography, flexography or other printing processes at step 26.

As noted above, lithographic and other forms of printing require the addition of reducing solvents to the varnish, in which case additional drying stations may be necessary for removal of the solvents prior to lamination.

The selectively coated substrate 24 and the transfer agent are laminated at step 28. More particularly, the respective webs of substrate 24 and transfer agent 20 are brought together in face-to-face

relationship between a pair of rollers and pressure is applied to laminate substrate 24 to transfer agent 20. The pressure required and the types of rollers used for lamination are described in U.S. Patent No. 4,215,170.

Subsequent to lamination the varnish is cured at step 30. In U.S. Patent No. 4,215,170, curing was allowed to occur naturally in approxinmately 24 hours or the curing was speeded up by the application of heat or the exposure to radiation. Each of these curing methods required at least a minimal interval between lamination and separation, thus delaying processing of the final product. The instant invention eliminates this disadvantage. More particularly, the electron beam curing apparatus shown in block diagram form at 30 can be of the type manufactured by Energy Sciences, Inc., 8 Gill Street, Woburn, Massachusetts 01801. This apparatus operates on the principal that when accelerated electrons penetrate into material they lose speed and transfer their energy into the material to be treated. The transferred energy excites molecules and forms a cloud of secondary electrons and free radicals which initiate chemical chain reactions in specific materials. There are two major applications of electron beam treatment, the simplest involves cross-linking and vulcanization, i.e., bonding between adjacent polymer chains and the second

involves electron initiated free radical polymerization.

The electron beam curing apparatus with which we are here concerned consists of several main elements.

The source of the electrons is a heated filament, the cathode. From here the electrons are accelerated, in vacuum, towards an electron transmissible window, which represents a grounded anode. A high voltage potential applied between the cathode and the anode accelerates the emitted electrons close to the speed of light.

The window, a thin metal foil, separates vacuum in the accelerator from atmospheric pressure in the treatment zone. The acceleration is done in an evacuated environment to avoid collisions with gas molecules and to prevent cathode oxidation.

There are two different types of industrial electron accelerators. An earlier design utilizes a pencil-shaped beam of electrons from a point source which is accelerated through a multistage accelerator tube and then scanned by an electromagnetic field through the window over the width of the product to be treated. This type of equipment is normally used for applications above 300 kV. Later designs, based on a linear cathode, generate a curtain of electrons over the entire product width without the need of scanning

the beam. The electron beam curing apparatus discussed above is described in a 1979 publication of Energy Sciences Incorporated entitled "ELECTRO CURTAIN".

With the electron beam curing process described above, the varnish coating is cured by exposure for a few milliseconds to the curtain of electrons without the use of heat. Since the product is completely, and essentially instantaneously cured, it is immediately available for further processing.

A slight heat build-up due to the energy transfer of the electrons and the chemical action can be observed. Normally, the heat build-up will not exceed a few degrees depending on the curing dose and the thickness of the reactive layer. Thus the equipment for electron beam curing can be described as a "cold oven" in which the reaction is initiated by the creation of free radicals by high energy electrons rather than by thermal effects.

The particular dose or treatment level required to cure a particular product depends on the type of material being cured and the thickness of the material.

Typically, a dose of between 1 and 6 megarads will be used, depending on the material and thickness of the varnish or adhesive, as well as the substrate and the transfer agent. Typically also, the voltage of the beam using the equipment described depends on the

thickness of the substrate that the beam is required to penetrate. Therefore it is preferable to cure through the transfer agent or film, since it is thin and consistent, rather than through the substrate, which is coarse and inconsistent in thickness.

The present invention is further illustrated by the following examples. All particulars and percentages in the examples, as are those in the specification and claims, are by weight unless otherwise specified.

EXAMPLE 1

A varnish of the following composition:

- Dekraken XD 8008-4 (Dow Chem.)	16
- TMPTA (Celanese Corp.)	38
- HDDA (Celanese Corp.)	35
- Stabilizer MARK 275 (Witco Chem.)	1

having a viscosity of 24 seconds measured with a cup (Ford Nr. 4) is printed on a 30 micron thick transfer agent of untreated biaxially oriented polypropylene film which has been vacuum metallized prior to the varnish coating.

The transfer agent is laminated at a speed of 40 to 50 meters/minute with a 80 gr/sqm woodfree coated paper substrate and passed under the electron beam of the

unit described hereinabove. The varnish is polymerized and the transfer agent and the substrate are immediately delaminated.

The transfer agent is clean and may be reused in the process. The metallized finished product is dry, has a specular surface, and can immediately be subjected to further processing, if desired.

EXAMPLE 2

A varnish designated CD 4336-51 (Lord Corp.) having a viscosity of 87 seconds in a number 2 Zahn cup, is substituted for the varnish composition given in Example 1 in the procedure described in Example 1. A dose of 2 Mrad electron beam radiation is used to cure the CD 4336-51 varnish.

EXAMPLE 3

The preparation of a metallized substrate in register is performed on a six color gravure press which has been installed with a laminating/electron beam/ delaminating unit between the first and second printing units.

A varnish of the following composition:

- Derakane XD 8008-04 (Dow. Chem.) 50
- TMPTA (Celanese Corp.) 30
- HDDA (Celanese Corp.) 10
- Stabilizer MARK 275 (Witco Chem.) 1
- Ethyl Alcohol 45

is printed in a design at a speed of 50 meters/minute on a woodfree coated substrate and dried in an oven at 100°C, but not cured. At the end of the drying step, the varnish-printed paper is laminated with a vacuum metallized oriented polyethylene film (transfer agent), passed under the electron beam in order to polymerize the varnish, and delaminated immediately thereafter, before entering the second printing unit.

The metallic design is overprinted in-line with a yellow transparent ink to give a specular gold effect.

EXAMPLE 4

In the process of Example 3, a varnish of the following composition is used:

- Resin 3810 (W.R. Grace) 54
- HOODA (Celanese) 6
- Toluene 40

This varnish, as prepared, has a viscosity of 21 seconds in a number 2 Zahn cup. The varnish is printed on a woodfree coated paper as described above and then

dried in an oven at about 70°C to increase the viscosity of the varnish to about 90 Pascal-seconds (Pa·s). The dried, but uncured, varnish-printed substrate is laminated to the metallized transfer agent, passed through the electron beam curing unit where the varnish is cured with a dose of 2 Mrad, and immediately delaminated to separate the now metallized substrate from the reusable transfer agent. As the substrate is separated from the transfer agent, it proceeds directly into the second print unit where the metallized design is overprinted, in substantial registry, with a yellow ink to give a specular gold effect.

EXAMPLE 5

A varnish of the following composition:

- STF-1237 (Reichhold)	56.5
- HDODA (Celanese)	12.0
- Toluene	31.5

having a viscosity of 24 seconds in a number 2 Zahn cup is printed in a design by the same procedure as described in Examples 3 and 4. This varnish is dried, however, to achieve a viscosity on the order of 7 Pa·s prior to entering the laminating/electron beam curing /delaminating unit. Again, a 2 Mrad dosage of electron beam radiation is used to substantially

instantaneously cure the varnish so as to permit immediate delamination of the reusable transfer agent and uniterrupted travel of the metallized substrate into the second printing unit. At the second printing unit, the metallized design is overprinted, in substantial registry, with an orange ink to give a specular copper effect.

EXAMPLE 6

A serigraphic impression is realized with an ink of the following composition:

- Ebecryl 584 (Union Chemical Belge)	25
- Ebecryl 830 (Union Chemical Belge)	25
- HDDA (Celanese Corp.)	5
- Modaflow (Monsanto)	1
- $CaCo_3$	6

The printing is performed on a coated board of 120 grams/sqm. The printed substrate is immediately laminated with a vacuum metallized oriented polypropylene film and polymerized with the electron beam curing unit. The delamination takes place immediately after the drying operation.

EXAMPLE 7

A varnish designated KC80-384 (Sun, GPI) is printed by lithography on a coated board. The printed substrate

is immediately laminated with a vacuum metallized, biaxially oriented, untreated polypropylene film and passed through the electron beam curing unit where it is cured with a dose of 3 Mrad electron beam radiation. The polypropylene film is immediately delaminated from the coated board.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in this art without departing from the spirit of the invention.

CLAIMS:

1. A process for the metallization of a substrate employing a reusable transfer agent comprising the steps of;

depositing on said transfer agent a film of metal particles of the order of magnitude of substantially less than 1000 Å (0.1µm) in thickness,

coating a portion of at least one of said substrate and said metallized transfer agent with electron beam-curable varnish,

laminating said substrate and said transfer agent together before said varnish is cured,

curing said varnish substantially instantaneously with electron beam radiation and

separating said transfer agent from said substrate immediately after said curing step is completed.

2. The process as claimed in claim 1 wherein said transfer agent is a resin selected from the group consisting of polypropylene, polyethylene, polyvinyl chloride, polyamide and regenerated cellulose.

3. The process as claimed in claim 1 or claim 2 wherein said metal particles are of metals selected

from the group consisting of aluminum, silver, gold, copper, nickel, tin and platinum and alloys of said metals.

4. The process as claimed in any preceding claim wherein said varnish is coated in a particular design not covering the entire surface of said substrate.

5. The process as claimed in any preceding claim wherein said substrate is selected from the group consisting of paper, cardboard, wood, leather and plastic.

6. The process as claimed in any preceding claim wherein said electron beam curing step polymerizes said varnish.

7. A metallized substrate formed by the process of any preceding claim.

8. A process for producing a specular metallic coating on at least predetermined portions of a substrate, the process comprising the steps of:

depositing a thin film of metal particles

on a transfer agent;

coating said at least a predetermined portion of at least one of said substrate and said metallized transfer agent with an electron beam-curable varnish;

laminating said substrate and said metallized transfer agent together before said varnish is cured to form a laminated product;

exposing said laminated product to electron beam radiation so as to substantially instantaneously cure said varnish;

delaminating said transfer agent from said substrate substantially immediately after performing said step of exposing; and

printing in substantial registry with the metallic coating on said at least a predetermined portion of said substrate.

9. The process as claimed in claim 8 wherein said coating step and said printing step are performed by use of a gravure press.

10. The process as claimed in claim 8 or claim 9 wherein said thin film of metal particles has a thickness of the order of magnitude of substantially less than 1000 Å (0.1μm).

11. The process as claimed in any one of claims 8 to 10 wherein said transfer agent is a resin selected from the group consisting of polypropylene, polyethylene, polyvinyl chloride, polyamide and regenerated cellulose.

12. The process as claimed in claim 11 wherein said transfer agent has a structured surface, thereby causing said metallic coating to be formed as a replica of the structured surface of said transfer agent.

13. The process as claimed in any one of claims 8 to 12 wherein prior to said exposing step said laminated product is oriented so that the transfer agent side is first exposed to the source of electron beam radiation.

14. The process as claimed in any one of claims 8 to 13 further comprising the steps of:

diluting said varnish with a solvent prior to said coating step; and

evaporating at least a portion of said solvent so as to increase the viscosity of said varnish prior to said laminating step.

15. The process as claimed in claim 14 wherein said evaporating step comprises drying said varnish in an oven at an elevated temperature.

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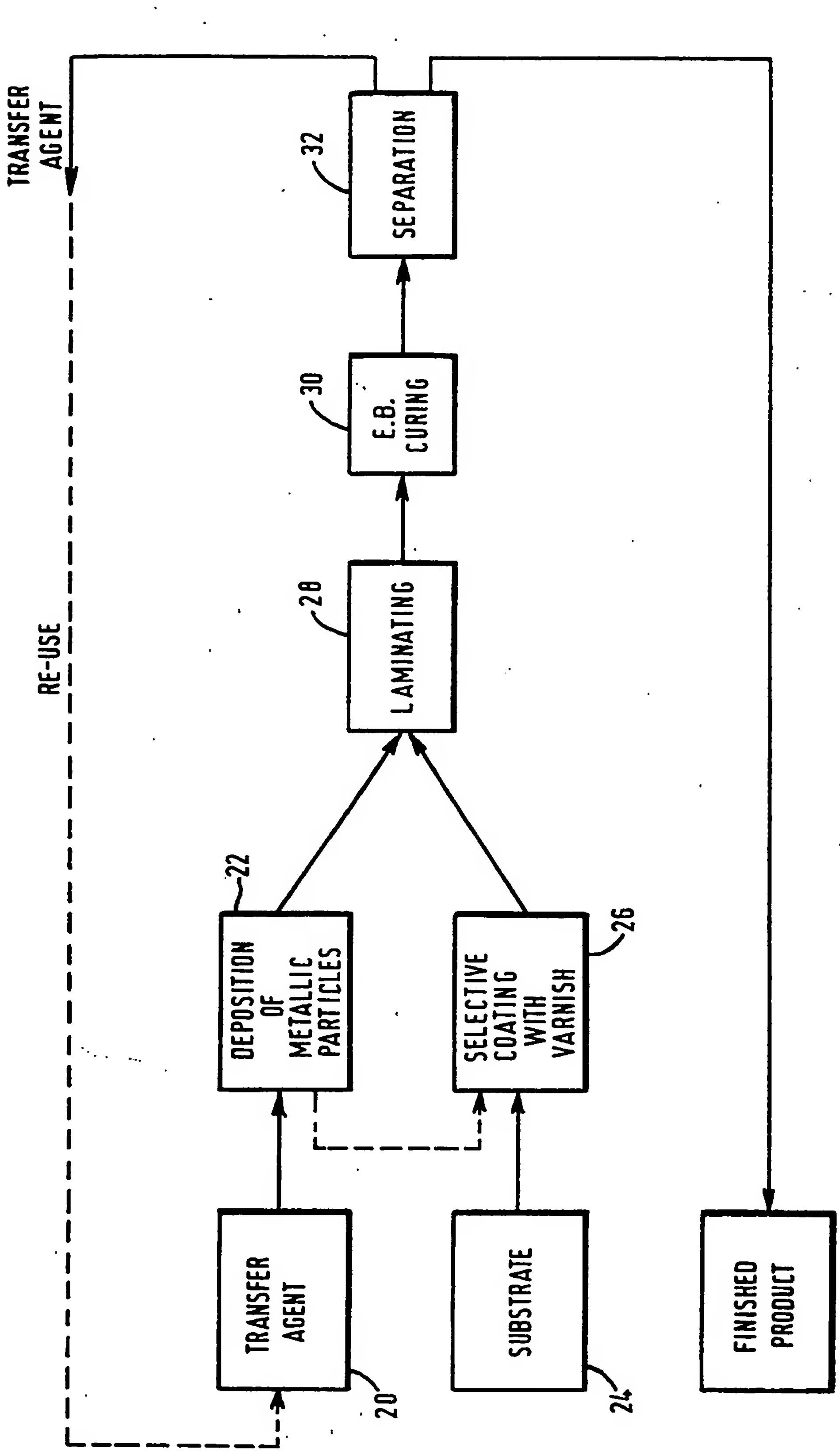
TRANSFER AGENT
20
DEPOSITION OF METALLIC PARTICLES
22
SUBSTRATE
24
SELECTIVE COATING WITH VARNISH
26
LAMINATING
28
E.B. CURING
30
SEPARATION
32
FINISHED PRODUCT
TRANSFER AGENT
RE-USE

European Patent Office

EUROPEAN SEARCH REPORT

0130659

Application number

EP 84 30 0108

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 52, no. 1, July 1981, page 124, no. 1032, Appleton, Wisc., US & JP - A - 80 163 294 (T. TAKAHASHI et al.) 19-12-1980 * Lines 6-9 of the abstract *	1,3,5-7,13	B 44 C 1/14 B 05 D 3/06 D 21 H 1/12

D,Y	US-A-4 215 170 (D.E.V. OLIVA) * Whole document *	1,5	
A		2-4,7-11,13-15	

Y	EP-A-0 050 398 (SCOTT PAPER) * Figure; claims 1,5,7-9; page 6, line 32 - page 7, line 28 *	1,5	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
A		6,12	D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-05-1984	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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